Supplementary Material:

Evaluating Electrocatalytic Activity for Hydrogen Evolving Cobalt and Nickel Complexes in Solution

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Section S1. Bulk Electrolysis Charge-Time Plots

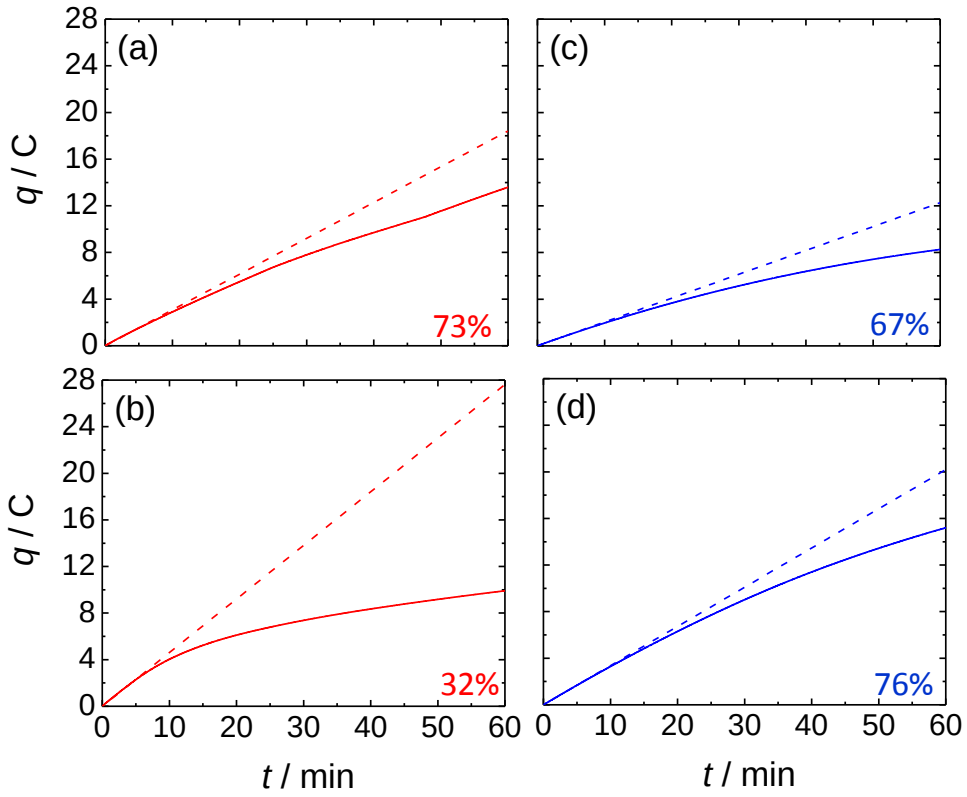

Figure S1. Bulk electrolysis measurements in a stirred solution of 0.3 mM of **1** (a, c) and **2** (b, d) in the presence of 5.2 mM TsOH (a, b) and 2,6-dichloroanalinium (c, d) measured at -1.01 V vs. Fc/Fc^{+}. The solid line is the measured charge as a function of time. The dashed lines are extrapolated from the first 360 s of each plot, and represent the theoretical charge-time curves for a well-stirred system under steady-state control. The numbers in the bottom right corner of each plot are the percentage difference between the measured and theoretical charge at 60 mins. This analysis suggests a much larger deviation from linearity for **2** in TsOH than for **1** in TsOH or either **1** or **2** in 2,6-DCA, consistent with electrochemically-mediated degradation of **2** in TsOH. Note that the Faradaic efficiency averaged over 3-5 experiments for the reduction of 2,6-dichloranalinium by **1** is $\varepsilon = 99 \pm 3\%$, and by **2** is $\varepsilon = 98 \pm 4\%$.

Section S2. Attempted H_2 Oxidation with 6.

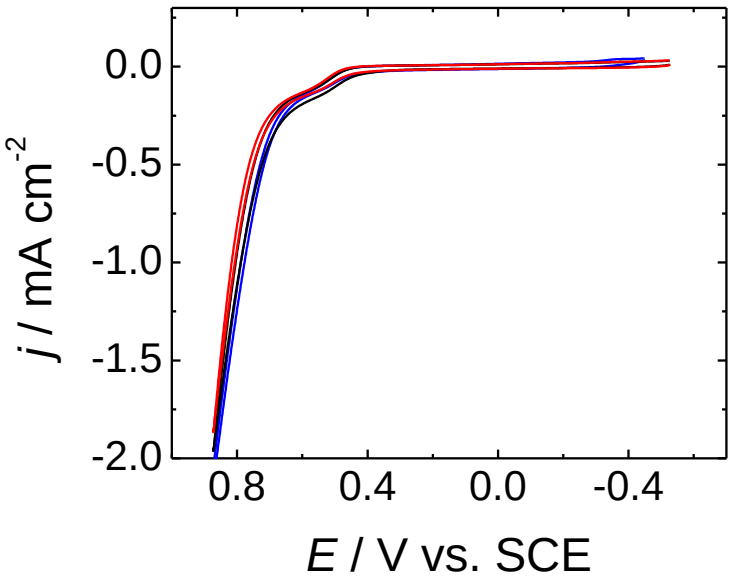

Figure S2. Cyclic voltammogram of 0.3 mM **5** with 0.25 mM Et_3N under Ar (black) and 523 psia H_2 (red). The blue line is in the presence of 240 mM Et_3N and under 531 psia H_2, but in the absence of **5**. (Supporting electrolyte is 0.1 M (nBu$_4$N)ClO$_4$ in CH_3CN, scan rate = 0.05 V/s)